

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENT
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

PCT Application
PCT/CN2005/000087

Applicant's or agent's file reference FPCH04160042		FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/CN2005/000087	International filing date (day/month/year) 19.Jan 2005 (19.01.2005)	Priority date (day/month/year) 19.Jan 2004 (19.01.2004)	
International Patent Classification (IPC) or national classification and IPC IPC⁷ C07C2/62 C07C2/70 C07C9/21 C07C9/14 C07C15/00			
Applicant CHINA PETROLEUM & CHEMICAL CORPORATION et al.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>3</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of <u>3</u> sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic _____), containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 18. Nov 2005 (18.11.2005)		Date of completion of this report 21. Dec 2005 (21.12.2005)	
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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/CN2005/000087

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of:
- ☐ international search (Rules 12.3(a) and 23.1(b))
- ☐ publication of the international application (Rule 12.4(a))
- ☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

- ☒ the international application as originally filed/furnished
- ☒ the description:
- pages 1-19 _____ as originally filed/furnished
- pages * _____ received by this Authority on _____
- pages * _____ received by this Authority on _____
- ☒ the claims:
- pages _____ as originally filed/furnished
- pages * _____ as amended (together with any statement) under Article 19
- pages * 1-3 _____ received by this Authority on 18. Nov 2005
- pages * _____ received by this Authority on _____
- ☐ the drawings:
- pages _____ as originally filed/furnished
- pages * _____ received by this Authority on _____
- pages * _____ received by this Authority on _____

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets/figs _____
- ☐ the sequence listing (*specify*): _____
- ☐ any table(s) related to sequence listing (*specify*): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets/figs _____
- ☐ the sequence listing (*specify*): _____
- ☐ any table(s) related to sequence listing (*specify*): _____

* If item 4 applies, some or all of those sheets may be marked "superseded."

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/CN2005/000087**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement:**

Novelty (N)

Claims 1-24

YES

Claims

NO

Inventive step (IS)

Claims 1-24

YES

Claims

NO

Industrial applicability (IA)

Claims 1-24

YES

Claims

NO

2. Citations and explanations (Rule 70.7)**1. Cited documents:**

D1: US6103947A(See the whole document, especially the example 1)

2. Novelty

Claim 1 claims a solid acid catalytic process for alkylating aromatic hydrocarbons or isomeric paraffin with olefin, which features that the solid acid catalyst contracts with hydrogen halide before it contacts with the raw materials mixture composed of aromatic hydrocarbons or isomeric paraffin, monoolefins and a compound containing strong electrically negative element as assistant;

None of the prior art disclosed or taught the processes of claims 1. Accordingly, the subject-matter of claim 1 is considered to be novel, that is, it is considered to meet the requirement of Article 33(2)PCT.

Based on the same reason, the dependent claims 2-24 are also considered to meet the requirement of Article 33(2)PCT.

3. Inventive steps

It seems that D1 is the most relevant document.

D1 disclosed an alkylating process of isomeric paraffin and olefin(pls see the example 1), which includes the following steps: 1) the solid acid catalyst loaded in the reactor was flushed with liquid isobutane containing 1000ppm chloride as sec-butyl chloride, 2) after completion of the flush, a feedstock containing isobutane, butene, and sec-butyl chloride was cut into the plant to perform the alkylation reaction;

The difference between D1 and claim 1 is that, in D1, the catalyst contacts with sec-butyl chloride before the alkylation, but in claim 1, it contacts with hydrogen halide before the alkylation;

Because Paul T. Barger et al. doesn't explain why to flush the catalyst with isobutane containing sec-butyl chloride, it is not evident for the skilled in the art to contact the catalyst with hydrogen halide before the alkylation reaction to improve the selectivity of the products such as TMP and to improve the stability of the catalyst.

Accordingly, the subject-matter of claim 1 is considered to involve inventive steps, that is, it fulfills the requirement of Article 33(3) PCT.

Based on the same reasons, the subject-matters of dependent claims 2-24 also fulfill the requirement of Article 33(3) PCT.

3. Claims 1-24 are considered to be industry applicable.

权 利 要 求

- 1、一种固体酸催化芳烃或异构烷烃与烯烃的烷基化反应方法，是将包括芳烃或 $C_4 - C_6$ 异构烷烃、 $C_2 - C_{18}$ 单键烯烃和作为反应助剂的强电负性元素化合物在内的反应物料与固体酸催化剂接触进行烷基化反应，其特征在于所说的固体酸催化剂在与反应物料接触前，先与卤化氢接触。
- 2、按照权利要求 1 的方法，其中在固体酸催化剂与反应物料接触前，所说卤化氢被包含在烃之中与所说催化剂相接触。
- 3、按照权利要求 2 的方法，其中所说包含卤化氢的烃是芳烃或异构烷烃。
- 4、按照权利要求 3 的方法，其中所说包含卤化氢的芳烃或异构烷烃是所说烷基化反应的原料。
- 5、按照权利要求 1-4 任何一项的方法，其中所说单键烯烃是 $C_3 - C_6$ 单键烯烃。
- 6、按照权利要求 1 的方法，所说的强电负性元素为卤素。
- 7、按照权利要求 3 的方法，所说的包含卤化氢的芳烃或异构烷烃中，卤化氢含量为 10 - 5000ppm。
- 8、按照权利要求 7 的方法，所说的卤化氢含量为 30 - 3500ppm。
- 9、按照权利要求 8 的方法，所说的卤化氢含量为 50 - 3000ppm。
- 10、按照权利要求 1-4 和 7-9 中的任一方法，所说的卤化氢为 HF 或 HCl。
- 11、按照权利要求 3 的方法，所说的包含卤化氢的异构烷烃为 $C_4 - C_6$ 异构烷烃中的一种或其混合物。
- 12、按照权利要求 11 的方法，所说的异构烷烃为异丁烷。
- 13、按照权利要求 1 的方法，所说的 $C_4 - C_6$ 异构烷烃为异丁烷。
- 14、按照权利要求 1 的方法，所说的芳烃为苯或萘。
- 15、按照权利要求 5 的方法，所说 $C_3 - C_6$ 单键烯烃为丁烯。
- 16、按照权利要求 1 的方法，其中所说的固体酸催化剂在与反应物料接触前，先与包含卤化氢的芳烃或异构烷烃接触的条件是：温度为 10 - 350℃，压力为 0.5 - 10.0MPa，包含卤化氢的芳烃或异构烷烃的重量空速为 0.2 - 8 小时⁻¹。
- 17、按照权利要求 16 的方法，所说的接触的条件为：温度为从芳烃

或异构烷烃的临界温度到 350℃, 压力为从芳烃或异构烷烃的临界压力到 10.0MPa, 包含卤化氢的芳烃或异构烷烃的重量空速为 0.5~8.0 小时⁻¹。

18、按照权利要求 1 的方法, 所说的烷基化反应条件为: 反应温度为 10~350℃, 反应压力为 0.5~10.0MPa, 芳烃或异构烷烃与烯烃的摩尔比范围为 2~200, 反应原料的重量空速为 0.1~20 小时⁻¹, 反应物料中含强电负性元素的化合物的含量为 10~5000ppm。

19、按照权利要求 18 的方法, 所说的烷基化反应条件为: 反应温度为从芳烃或异构烷烃的临界温度到 350℃, 反应压力为从芳烃或异构烷烃的临界压力到 10.0MPa, 芳烃或异构烷烃与烯烃的摩尔比范围为 10~90, 反应原料的重量空速为 0.5~8.0 小时⁻¹, 具有强电负性元素的化合物的含量为 50~3000ppm。

20、按照权利要求 1 的方法, 其中所说固体酸催化剂为负载型杂多酸催化剂、负载或不负载杂多酸盐催化剂、沸石分子筛催化剂、SO₄²⁻/氧化物超强酸催化剂、负载型 Brönsted-Lewis 共轭固体超强酸催化剂、Brönsted 酸或 Lewis 酸处理的氧化物或分子筛催化剂。

21、按照权利要求 1 的方法, 其中所说固体酸催化剂为负载型杂多酸催化剂、负载或不负载杂多酸盐催化剂、负载型 Brönsted-Lewis 共轭固体超强酸催化剂、Brönsted 酸或 Lewis 酸处理的氧化物催化剂。

22、按照权利要求 20 或 21 的方法, 其中所说负载型杂多酸催化剂由多孔无机载体和一种杂多酸组成, 其中所说杂多酸通式为 H_{8-n}[AM₁₂O₄₀], 其中 A 为 P 或 Si, M 为 W 或 Mo, n 为 A 的价态, 其值为 4 或 5; 其中所说负载型杂多酸盐催化剂由多孔无机载体和一种杂多酸盐组成, 其中所说杂多酸盐通式为 H_{8-n-mx}N_x[AM₁₂O₄₀], 其中 N 为选自碱金属离子、铵离子、碱土金属离子和 IIIA 族金属离子, m 为金属离子的价态, x 为 0<mx<4 之间的任意数, A 为 P 或 Si, M 为 W 或 Mo, n 为 A 的价态, 其值为 4 或 5; 所说多孔无机载体为包括活性炭、氧化硅、氧化铝、氧化镁、氧化钛、天然或人工合成的硅铝酸盐沸石、碳纤维和天然粘土在内的常规多孔无机载体, 或者是它们的混合物。

23、按照权利要求 22 的方法, 其中所说多孔无机载体为氧化硅、氧化铝或者它们的混合物。

24、按照权利要求 20 或 21 的方法, 其中所说负载型 Brönsted-Lewis

共轭固体超强酸由 40-95 重%的一种多孔无机载体和负载其上的 1-60 重%的一种杂多酸以及 0.3-15 重%的一种路易斯酸所组成；所说杂多酸和多孔无机载体的定义与权利要求 22 中对杂多酸和多孔无机载体的定义相同；所说路易斯酸选自 AlCl_3 、 BF_3 或者 XF_5 ，其中 X 为 P、As、Sb 或者 Bi。